

5. Nitrous Oxide and Halocarbon Division

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5.1. CONTINUING PROGRAMS

5.1.1. FLASK SAMPLES

Air samples were collected in pairs and analyzed as in the past with one change. In mid-June, flasks started being humidified by filling them with air flowing through a bubbler prior to their being returned to the field sites. This conditioning step is an attempt to passivate the flask walls and minimize surface chemistry for compounds like carbon tetrachloride (CCl_4). Filling instructions were revised and, therefore, flasks are purged 50% longer. The efficacy of these changes is currently being assessed.

Other minor program changes also instituted in June included: (1) using flow meters with the larger flasks during filling so that flushing rates are equal, (2) conducting field site pump performance tests periodically, and (3) checking flask pressures after filling and before analysis on each instrument. More 0.85 and 2.5 L flasks were added; therefore, instruments such as the gas chromatograph-mass spectrometer (GC-MS) were guaranteed sufficient air for analyses.

A maintenance trip was made to Alert, Northwest Territories, Canada, in May to install an air sampling inlet system [Montzka *et al.*, 1992]. The air inlets are at 10 m and 5 m on the north tower. Flasks are currently filled only from the highest inlet. SPO is the other field site where flasks are filled through this type of inlet system.

A year of analyzing the flask air samples on the original electron capture-gas chromatograph (EC-GC) and the Autoflask system is complete. The Autoflask system is patterned after the Radiatively Important Trace Species (RITS) GC in situ system [Montzka *et al.*, 1992]. This comparison showed some weaknesses in the Autoflask flask inlet plumbing and system control software. Necessary changes were made, and an additional period of overlapping analyses will be done before the old GC is retired from service.

Chlorofluorocarbon (CFC) -11 and -12 concentration growth rates continue to decrease as their expected usage diminished [Elkins *et al.*, 1993]. In 1993 the CFC-11 growth rate was about 1 ppt yr^{-1} with CFC-12 being 10 ppt yr^{-1} (Figure 5.1).

The growth rate of nitrous oxide (N_2O) has decreased since 1991 from about 1 ppb yr^{-1} to 0.5 ppb yr^{-1} . The yearly global means of measurements from flasks collected at seven sites show that mixing ratios of N_2O appear to have leveled off in 1993 (Figure 5.2). The cause of this decrease in the growth rate is unknown and may be the result of many mitigating factors. Worldwide use of

fertilizer has decreased by over 10% which will lessen its source of N_2O . Since the eruption of Mt. Pinatubo in June 1991, northern hemispheric temperatures have decreased by 0.5°C ; this could reduce the N_2O amount produced by bacteria that are strongly influenced by temperature change. Since the summer of 1990 through the end of 1993, the SOI was consistently negative. A large negative anomaly (<-1) indicates a warming event in the tropical ocean that usually means less equatorial upwelling and less flux of deep water N_2O into the atmosphere. Two such events were recorded in the summer of 1991 and summer of 1992 through the spring of 1993.

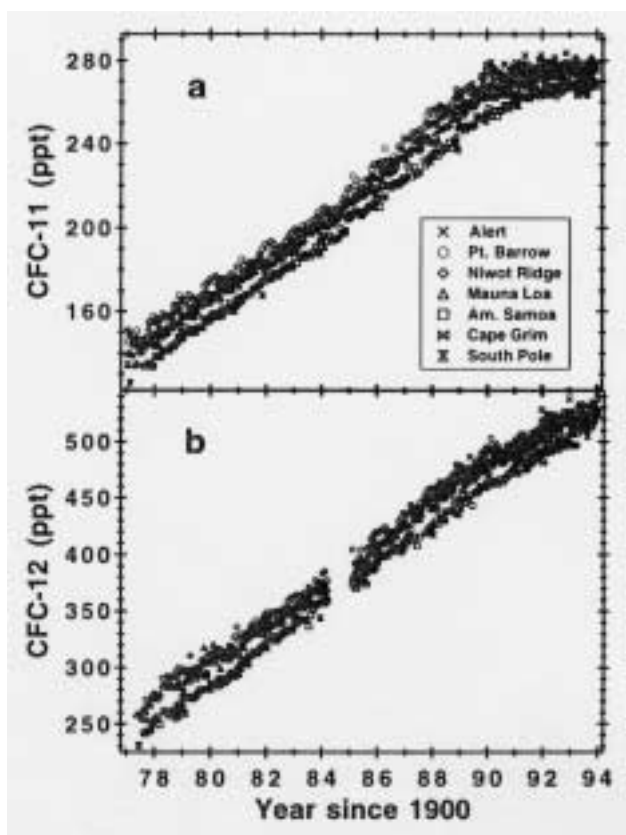


Fig. 5.1. Monthly means of atmospheric mixing ratios measured from flasks collected at the seven NOAA flask network sites for (a) CFC-11 and (b) CFC-12. Values are reported as dry mole fractions [Elkins *et al.*, 1993] in parts-per-trillion (ppt). A color figure is available from the authors.

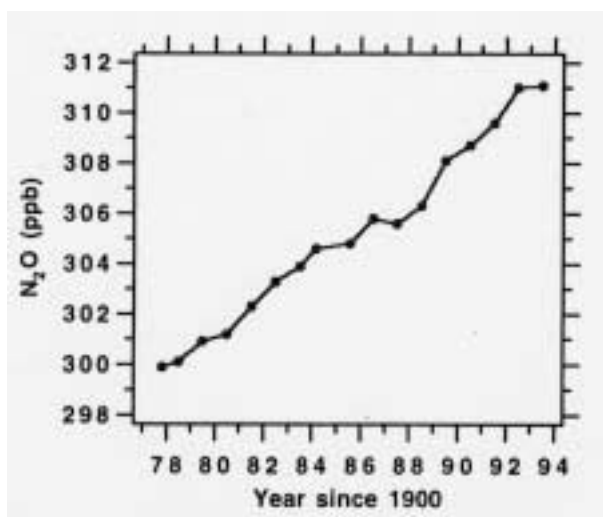


Fig. 5.2. Yearly global means of atmospheric N₂O mixing ratios collected at the seven NOAA flask network sites. Values are reported as dry mole fractions in parts-per-billion (ppb).